CLUSTER INTENSITY AND VELOCITY MEASUREMENTS IN CONDENSED FLOWS

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September 1974

Final Report for Period March 28 — May 11, 1973

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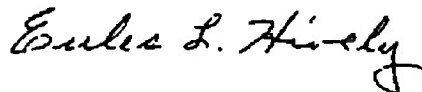...   .   ..
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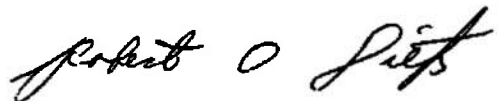Qualified users may obtain copies of this report from the Defense Documentation Center.

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
I. REPORT NUMBER AEDC-TR-74-38	2. GOVT ACCESSION NO.	3 RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* CLUSTER INTENSITY AND VELOCITY MEASUREMENTS IN CONDENSED FLOWS		5 TYPE OF REPORT & PERIOD COVERED Final Report - March 28 to May 11, 1973
		6. PERFORMING ORG. REPORT NUMBER
7 AUTHOR(s) A. B. Bailey - ARO, Inc.		8. CONTRACT OR GRANT NUMBER(s)
9 PERFORMING ORGANIZATION NAME AND ADDRESS Arnold Engineering Development Center(DYFS) Air Force Systems Command Arnold Air Force Station, Tennessee 37389		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Program Element 62101F Project 7635
11. CONTROLLING OFFICE NAME AND ADDRESS Arnold Engineering Development Center(DYFS) Air Force Systems Command Arnold Air Force Station, Tennessee 37389		12. REPORT DATE September 1974
		13 NUMBER OF PAGES 33
14 MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)*		15 SECURITY CLASS. *(of this report)* UNCLASSIFIED
		15a DECLASSIFICATION·DOWNGRADING SCHEDULE N/A

16 DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17 DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

Available in DDC

19 KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

spectrometer
molecular beams
cryopumping
skimmers

vacuum chambers
expansion (free-jet)
gases

20 ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The objective of the present investigation has been to obtain further information concerning the condensation process in expanding flows. To this end, molecular beams formed from expansions of argon, nitrogen, carbon dioxide, nitric oxide, krypton, and a 10-percent krypton/argon mixture have been analyzed with a quadrupole mass spectrometer and a metastable velocity analyzer. By varying the energy of the ionizing electrons, it has been found that (1) at low source pressures, it can be assumed that the measured

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20.   Abstract (Concluded)

dimer intensity corresponds to that occurring in the beam; and
(2) at high source pressures, i.e., where massive condensation
has occurred, the dimer signal is largely dependent on the
energy of the ionizing electrons. Also, it has been found that
the source pressure at which trimers, tetramers, etc., are first
observed is in good agreement with the pressure at which the
velocity increases. This observation, together with cluster size
measurements made elsewhere with different experimental techniques,
suggests that the pressure at which the velocity increases is
related to the onset of massive condensation in the expansion.
The variation of the source pressure at which massive condensation
occurs with source diameter and temperature has been summarized
for argon and nitrogen.

AFSC
Arnold AFS Tenn

PREFACE

The work reported herein was conducted by the Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), at the request of Air Force Cambridge Research Laboratories (AFCRL), Bedford, Massachusetts. The scope of the project has been coordinated with Dr. D. Golomb of AFCRL. The results were obtained by ARO, Inc. (a subsidiary of Sverdrup & Parcel and Associates, Inc.), contract operator of AEDC, AFSC, Arnold Air Force Station, Tennessee. The work was done under ARO Project No. VF233. Data reduction was completed on August 13, 1973, and the manuscript (ARO Control No. ARO-VKF-TR-74-8) was submitted for publication on January 15, 1974.

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ILLUSTRATIONS

1.0 INTRODUCTION

During the past 15 years or so, a considerable theoretical and experimental effort has been devoted to the problem of producing high-intensity molecular beams. These beams have been formed by skimming from the core of a free-jet expansion. Bossel (Ref. 1) has identified the characteristics that a conical skimmer should possess in order to produce an intense, near-isentropic and well collimated beam. Recently, some studies have been made of the formation of molecular beams using cryoliners and cryopumped skimmers and collimators (Refs. 2, 3, 4, and 5). These studies have shown that the effects of skimmer interference on the properties of the molecular beam can be significantly reduced through the use of cryopumped liners and skimmers. It has been shown (Refs. 3 and 4) that, when condensation occurs in a free-jet expansion, the properties of a beam formed with a non-pumping conical skimmer are significantly different from those formed with a cryopumping skimmer. It has been postulated (Ref. 4) that, when molecular clusters impact upon a non-pumping skimmer, the resulting fragments are predominantly monomers. These monomer fragments reflect into the incident beam and effectively attenuate the lighter species in the incident beam. It has been found that these attenuation effects are considerably reduced when cryopumped skimmers are used. This is a significant result in that molecular beam facilities have been used to (1) establish criteria for the onset of condensation in expanding flows (e.g., Refs. 2, 3, and 6), and (2) further the understanding of the chemical kinetics of cluster growth (e.g., Refs. 7, 8, and 9). To accomplish these objectives, it is necessary to ensure that the molecular sample being studied is not modified by the sample forming process, i.e., the skimmer. This requirement is most nearly achieved in a wholly cryopumped chamber. The purpose of the present investigation is to (1) obtain more information concerning the onset of condensation in expanding flows, and (2) extend the source pressure range over which cluster intensity measurements can be made to provide information from which the kinetics of cluster formation may be deduced.

2.0 APPARATUS

2.1 MOLECULAR BEAM CHAMBER MODIFICATIONS

A description of the von Kármán Gas Dynamics Facility (VKF) Aerodynamic Molecular Beam Chamber and the associated beam

detection systems is contained in Refs. 2 and 3. A schematic of the chamber configuration used in the present investigation is shown in Fig. 1. Several modifications have been made to the chamber to provide a greater degree of operational flexibility.
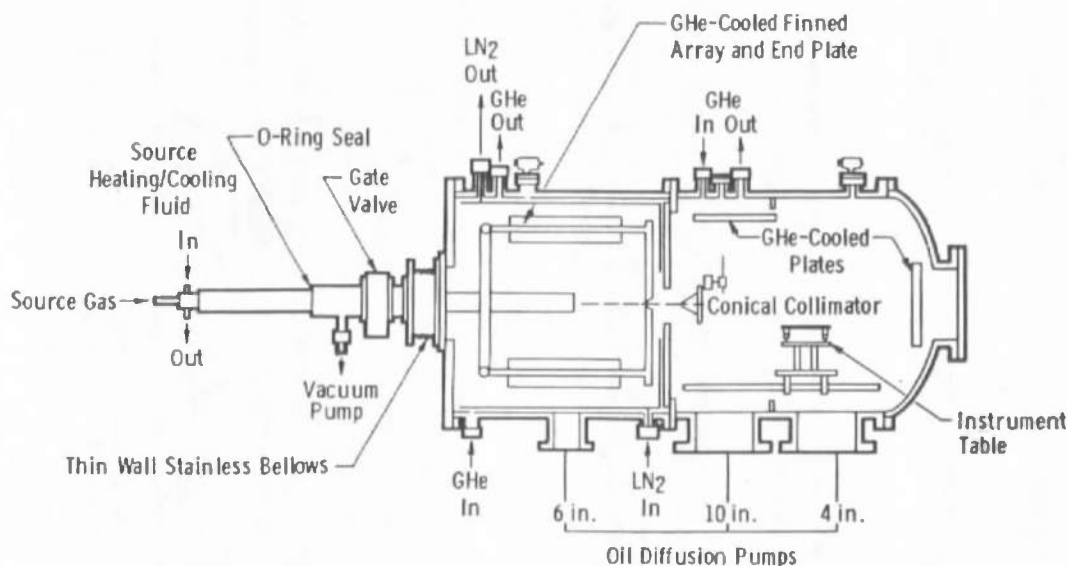

Figure 1. Schematic of AEDC-VKF molecular beam chamber.

The gaseous helium pumping system in the source section of the chamber, consisting of a copper cryoliner and a stainless steel skimmer with a 1.27-cm-diam orifice has been replaced with a finned aluminum array and end-plate having a 0.635-cm-diam orifice. The collimation section has been removed entirely in order to increase the length of the usable test volume. Its removal also permits the distance from the source to detector to be decreased, resulting in an increase in signal intensity at the detector. An instrumentation table mounted on linear bearings which permits motion parallel and normal to the longitudinal axis of the chamber has been installed in the test section. The mechanical and oil diffusion pumping system has been completely redesigned such that (1) the time to pump the chamber to 0.050 torr has been considerably reduced, (2) in the event of a power failure, the chamber is automatically isolated from the pumping system, and (3) the liquid-nitrogen traps on the 6- and 4-in. diffusion pumps have been replaced with a Freon® refrigerator which permits the continuous operation of these pumps. Chamber turn around time has been reduced through (1) the installation of two 500-watt lamps in the source section to reduce the warm-up time of the cryosurfaces, and (2) the installation of an air

ejector exhaust system which maintains the chamber pressure at 500
torr with a continuous inbleed of dry nitrogen.

2.2 DETECTOR SYSTEMS

Total beam intensity was measured with a miniature ionization gage
positioned on the beam centerline. A description of the modulated beam
detection system used to measure specie concentration in the molecular
beam is given in Ref. 2. It consists of (1) a mechanical beam chopper,
(2) an EAI quadrupole mass spectrometer (range from 2 to 600 atomic
mass units, AMU), and (3) a lock-in (narrow bandpass) amplifier. The
chopped molecular beam enters the ionization chamber of the mass
spectrometer. Ionized molecules are drawn into the quadrupole section,
which is tuned to a particular mass number. The resulting ion current
is amplified by an electron multiplier, which sends a pulsed signal to
the lock-in amplifier, which acts as a bandpass amplifier centered on
the chopper frequency. A light and a photocell detector, mounted at the
chopper wheel, provide the chopping frequency to the amplifier and keep
it synchronized with the actual molecular beam modulation frequency.
The lock-in amplifier increases the signal-to-noise ratio by amplifying
only those signals having the proper frequency and phase with respect
to the reference signal from the photocell. This amplified signal, re-
corded on a voltmeter, is a measure of the intensity of the mass num-
ber under 'investigation. In an earlier study (Ref. 3), the chopper wheel
had 20 equally spaced 1.9 by 0.16-cm slots in a 0.005-cm-thick steel
plate. This slot configuration was chosen so that measurements of
specie concentration and velocity distribution could be made with the
same chopper wheel. The sensitivity of both detection systems was re-
duced since this was not the optimum configuration for either system.
In the present study, the sensitivity of the specie concentration system
was increased by using a chopper with two slots giving an equal beam
on and off time. A further increase in system sensitivity was achieved
by (1) using a 17-stage CuBe electron multiplier as opposed to the 13-
stage multiplier used earlier (Ref. 3) (this 17-stage multiplier was fab-
ricated from two 13-stage multipliers.), and (2) increasing the multiplier
voltage from 3000 to 3900 volts.

The method of measuring velocity by detecting the metastable species
is shown schematically in Fig. 2 and was derived from Locke (Ref. 10).
The large aperture (1.5 cm square) electron source was fabricated from
a television picture tube gun by cutting off the last cylindrical element.
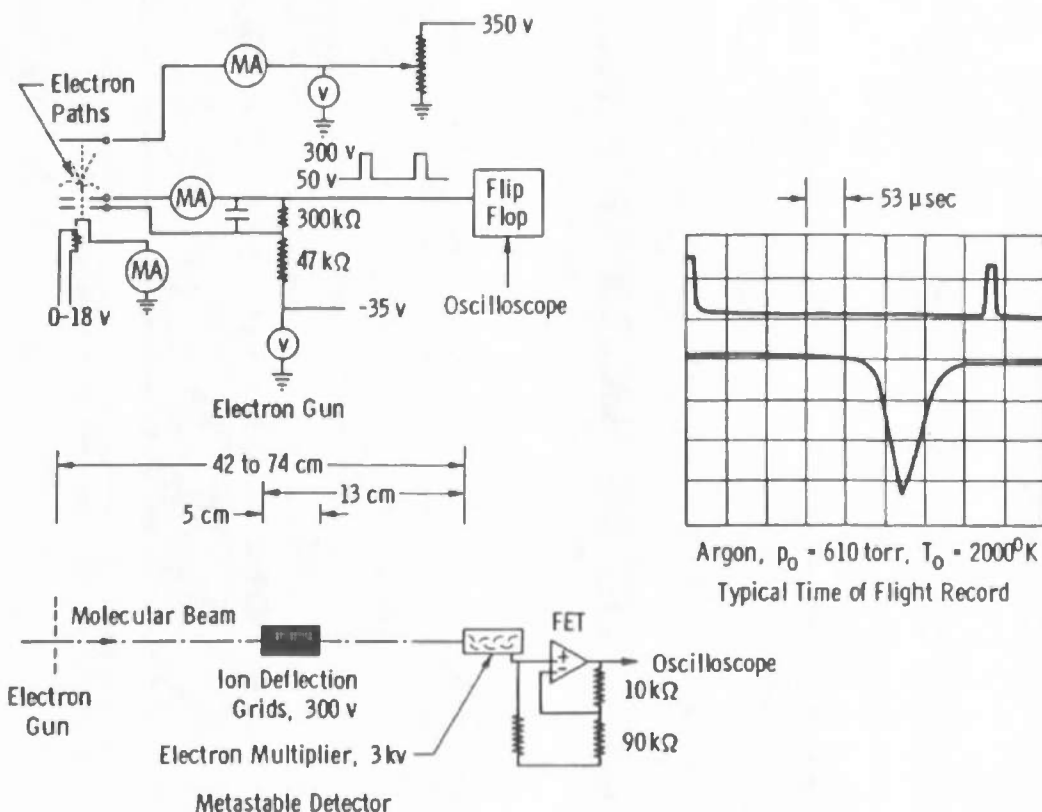Optimum metastable yields usually occur at relatively low electron

Figure 2. Metastable time of flight instrumentation.

energies (about 28 v for argon). A chopped metastable beam was gen-
erated by pulsing the electron accelerating voltage 1 to 200 μsec at in-
tervals comparable to the flight time. The time bases from a dual-
beam oscilloscope formed the pulses, the duration of which were
checked by a 10-MHz counter. A comparison of the times of flight for
two distances showed that the electronics delays were negligible. Ions
created in the flow by the electron beam were prevented from reaching
the detector by a deflection grid located between the electron gun and
the detector (Fig. 2). Figure 2 shows a typical metastable time-of-
flight record for argon.

The velocity corresponding to the time of maximum signal is the
most accurately determined flow property because the flight distance
and time can be measured directly. For high-speed ratio beams, this
velocity is a good approximation to the mean velocity of the beam. In
the present investigation, the variation of this velocity with source
diameter, pressure, and temperature was considered. No attempt was
made to determine the static temperature from the velocity profile.

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3.0 DISCUSSION OF EXPERIMENTAL RESULTS

3.1 INDICATORS OF CONDENSATION IN A FREE-JET EXPANSION

With the onset of condensation in a free-jet expansion, the following processes would be expected to occur as the source pressure is increased: (1) formation of molecular clusters, dimers, and trimers; (2) appearance of liquid droplets; and (3) formation of crystals. Audit (Ref. 11) has performed electron diffraction analyses of the particles existing in condensed supersonic molecular beams for various gases. In these studies, he reports on the identification of monomers, dimers, liquid droplets, and crystals. The source pressures at which these phases are identified in an argon flow are shown in Fig. 3. Also shown in Fig. 3 for similar source conditions are (1) the results of measurements of total monomer, dimer, trimer, and tetramer beam intensity
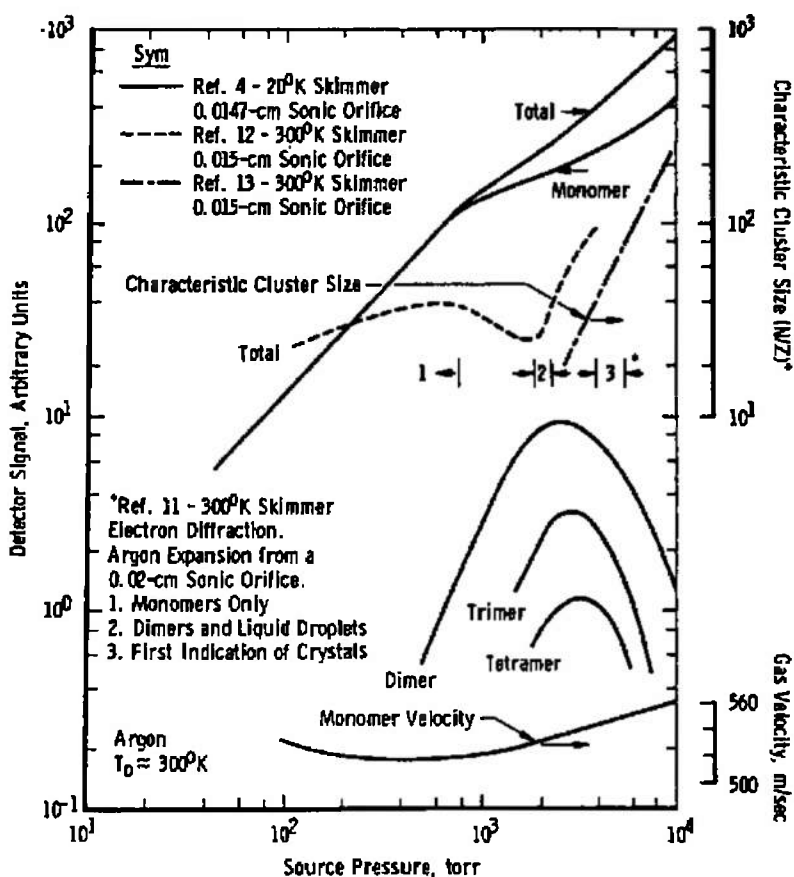
Figure 3. Indicators of condensation in free-jet expansions.

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and monomer velocity obtained in a previous investigation (Ref. 4); (2) total beam intensity measurements (Ref. 12); and (3) characteristic cluster size measurements (Ref. 13). In the present study, the pressure at which the monomer and total beam deviate and the monomer velocity increases are in reasonable agreement with Audit's observations.

Ruby (Ref. 2) observed a velocity variation of the form shown in Fig. 3. He suggested that this increase in velocity resulted from the addition of the heat of condensation to the flow. Sherman (Ref. 14) has shown theoretically that an increase in gas velocity would be expected after condensation has occurred. In the present study, it has been assumed that the pressure at which the velocity increases is indicative of condensation in the flow.

3.2 METASTABLE VELOCITY MEASUREMENTS

In an earlier experimental study (Ref. 4) the mass spectrometer was mounted such that it could be rotated about the center of the ionizing region. Thus, measurements could be made with the axis of the quadrupole section normal (side on) to and parallel (end on) to the axis of the molecular beam. Velocity distributions obtained for an argon flow with the quadrupole section parallel to the beam axis (end on) and tuned to mass numbers of 40 and 80 are shown in Fig. 4. When the
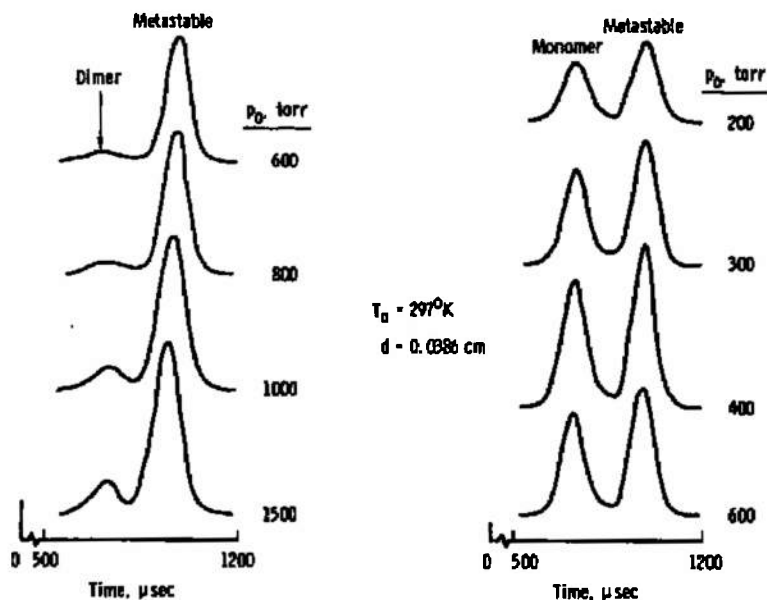

Figure 4. Velocity distribution for an argon beam.

mass spectrometer was tuned off the mass number for an argon cluster
or the radio frequency (RF) to the rods was turned off, a velocity dis-
tribution was obtained which corresponded to the second peak shown in
Fig. 4. It has been assumed that this signal results from the formation
of metastable argon atoms in the ionizing section of the mass spectro-
meter. These metastable atoms will not be accelerated by the electric
fields in the mass spectrometer. On the other hand, the monomer and
dimer ions will be accelerated by these electric fields. This velocity
difference in the quadrupole section accounts for the observed differences
in ion and metastable time of flight. Values of mean beam velocity de-
rived from distributions of this type (Fig. 4) are shown in Fig. 5. The
measurements of monomer velocity are in agreement up to the point
where condensation occurs (i.e., the pressure at which the monomer
velocity increases). Beyond this point, the measured beam velocity de-
pends on the mode of operation of the mass spectrometer, i.e., end-on
or side-on. The metastable velocity values appear to be in reasonable
agreement with the monomer velocity values obtained with side-on mode
of mass spectrometer operation. These various velocity measurements
can be explained if it is assumed that the condensed beam contains mono-
mers traveling at or in excess of the theoretical thermal velocity (excess
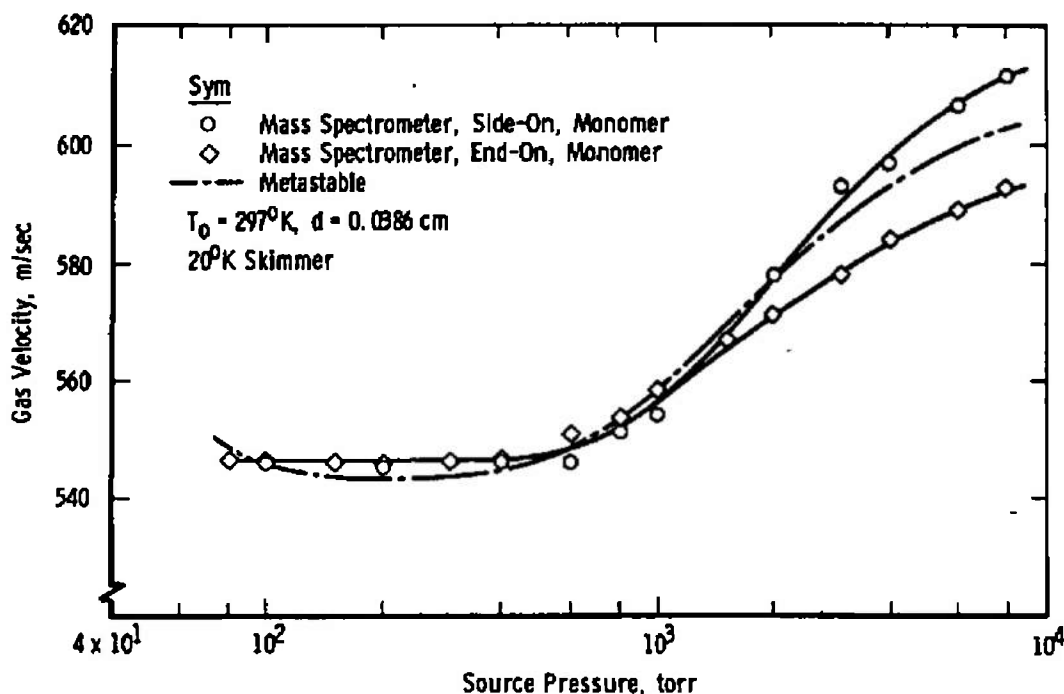velocity resulting from the addition of the heat of condensation to the

Figure 5. Argon mean beam velocity as a function of source pressure.

flow) and large clusters traveling at lower velocities. In the end-on mode of operation some of the large clusters can strike the mass spectrometer at the entrance of the quadrupole section. Some of the resulting fragments, primarily monomers, will be backscattered into the ionizing region where monomer ions and metastables, traveling at cluster velocity, will be formed. The ions will be drawn into the quadrupole section, and their net effect on the mean monomer velocity will be to lower it. The metastables formed from the backscattered debris cannot be extracted by the mass spectrometer so the derived metastable velocity should be a correct measure of the incident beam monomers.

It has been shown (Ref. 15) that a relative measure of beam intensity can be obtained by multiplying the oscilloscope deflection (Fig. 4) by the value of the beam velocity. Some monomer and metastable intensity values obtained in this way are shown in Fig. 6. From a comparison of the metastable and side-on monomer signals, it can be concluded that the metastable signals are directly proportional to the monomers in the incident beam. When there is significant condensation in the flow, the end-on monomer intensity is greater than that observed in the side-on mode reflecting the presence of cluster fragments discussed earlier.
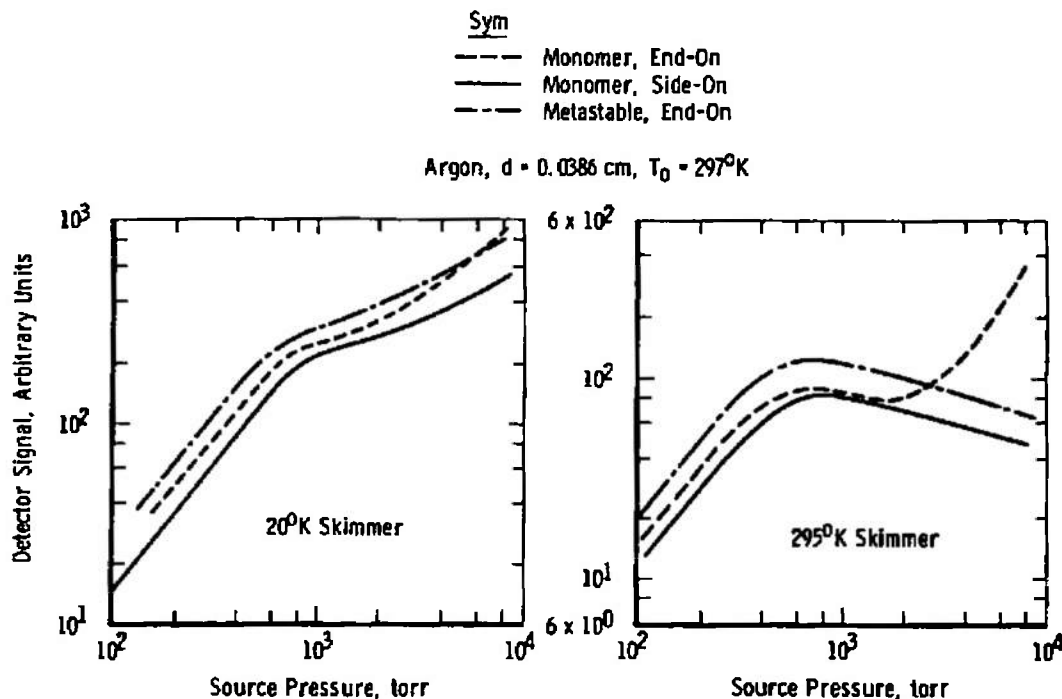

Figure 6. Relative intensity of monomer and metastable signals.

Some metastable velocity measurements obtained in the present study are shown in Fig. 7. These measurements indicate that beam velocity is independent of the duration of the electron beam (for times ranging from 2 to 200 μsec). For a pulse width of 50 μsec, velocity measurements were obtained with the 0.193-cm-diam collimator in and out of the beam. By arbitrarily matching these measurements (Fig. 8)
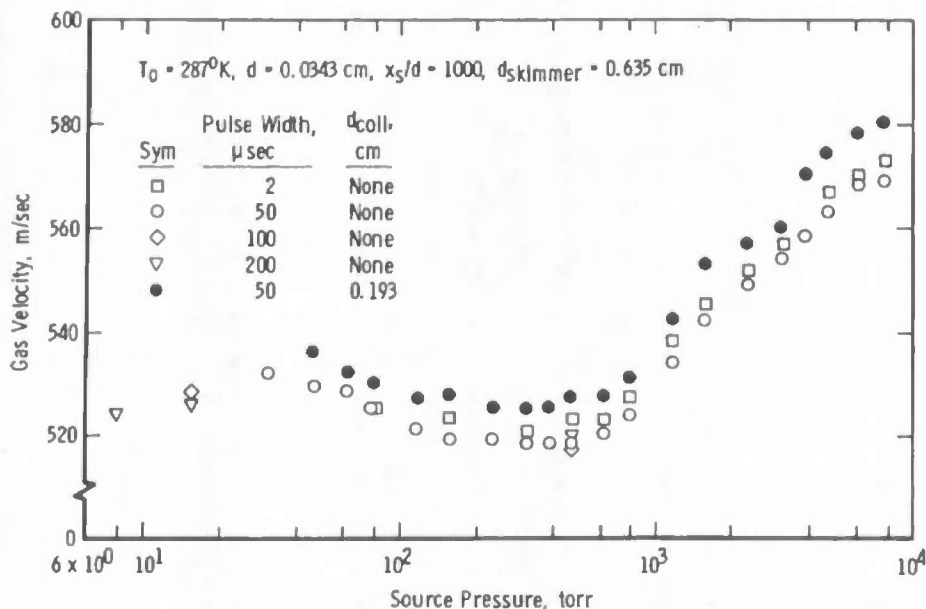

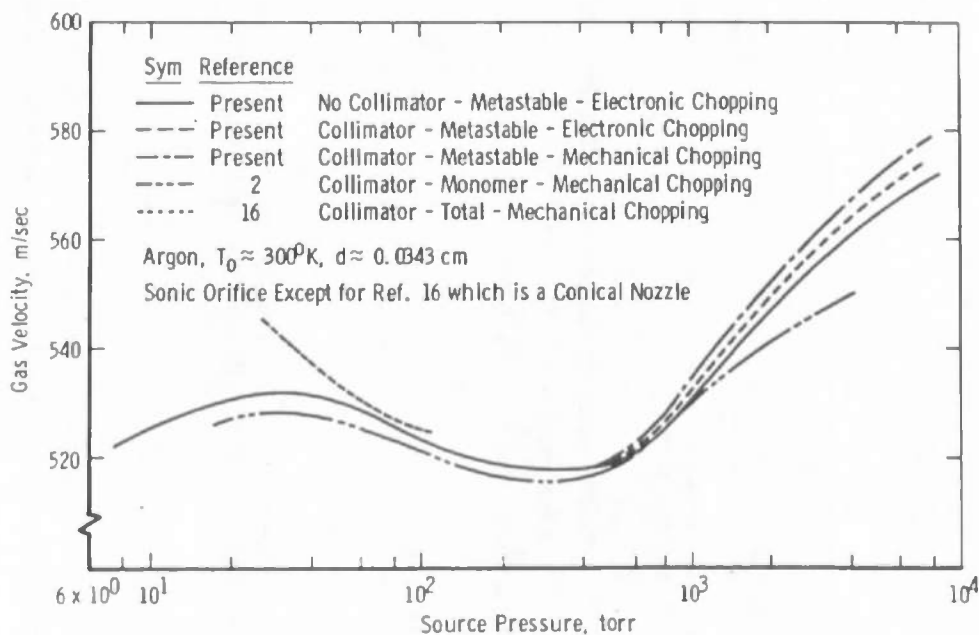Figure 7. Metastable argon velocity as a function of source pressure.

Figure 8. Comparison of argon velocity measurements.

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at low pressures, it can be seen that (1) the velocity is not dependent on the degree of beam collimation, and (2) there are no significant differences between the metastable data obtained with the mechanical chopper (Fig. 5) and the electronically pulsed beam. This indicates that the mechanical chopper does not significantly modify the velocity distribution of a condensed beam. Also shown in Fig. 8 are Ruby's data (Ref. 2) and some measurements made by Becker and Henkes (Ref. 16). (Both sets of measurements have been arbitrarily matched to the present data at low source pressures.)

All of these measurements (Fig. 8) indicate that there is a peak in the variation of velocity with source pressure at low source pressures. A similar peak has been observed in free-jet expansions of carbon dioxide (Fig. 9). Sherman (Ref. 14) has stated that, when the heat is initially added to a supersonic stream, the velocity decreases. This decrease in velocity results from an increase in the static temperature
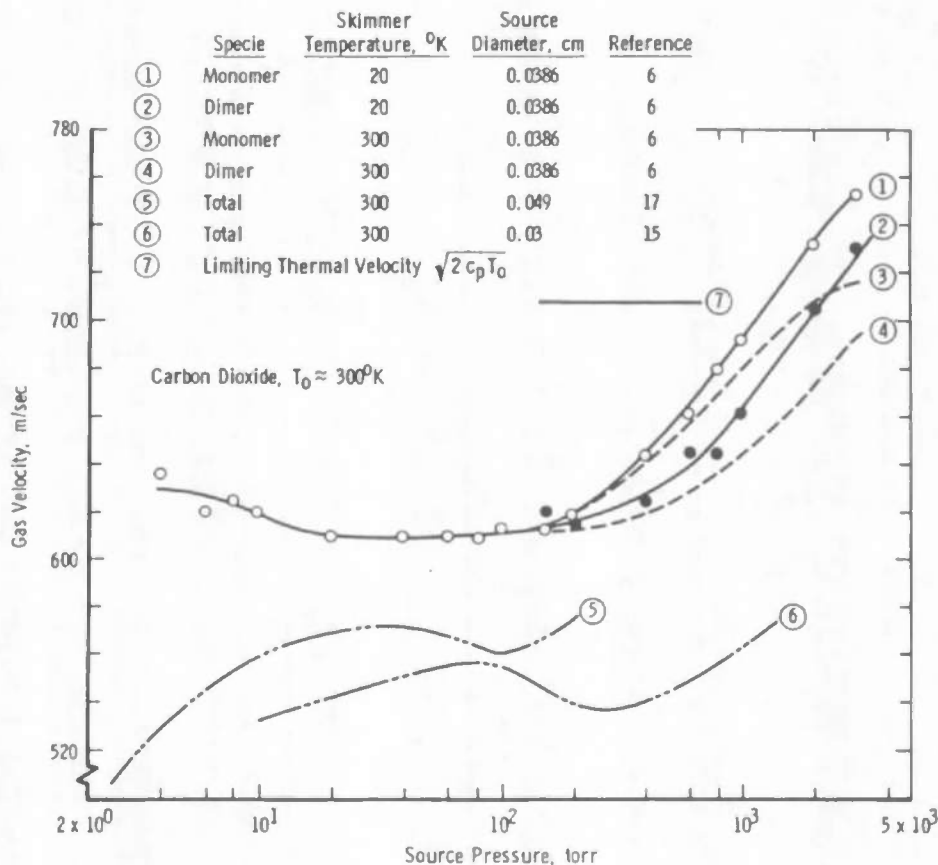

Figure 9. Comparison of carbon dioxide velocity measurements.

of the gas. As the quantity of heat added to the gas increases, a point
is reached where the increase in local static temperature has a smaller
effect on the stream velocity than the increase resulting from an increase
in the effective stagnation temperature. The experimental data appear
to support Sherman's (Ref. 14) description of the effect that heat addition
(in the form of the heat of vaporization) has on an expanding flow. Thus,
it may be more correct to assume that the peak in the velocity variation
is indicative of the onset of condensation rather than the pressure at
which the velocity increases. Considerably more experimental data
would have to be obtained before the validity of the foregoing assumption
can be determined.

The pressure at which the velocity increases for argon and nitrogen
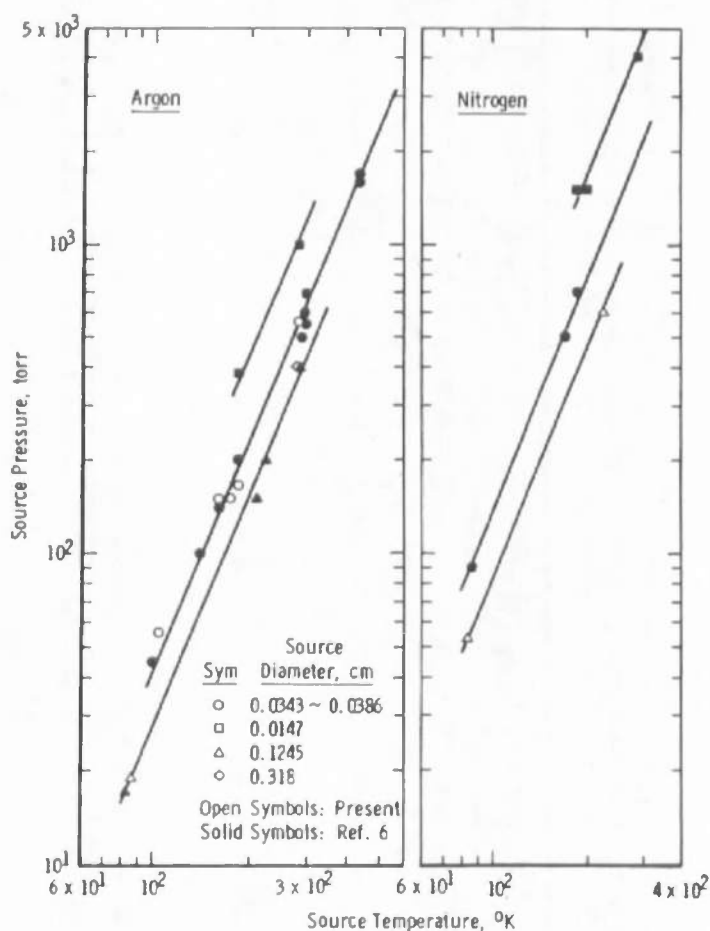expansions are summarized in Fig. 10 for the present investigation and

Figure 10. Source pressure at which gas velocity increases as a
function of source temperature and diameter.

that of Ref. 6. In the light of a comparison of these measurements with the results of electron diffraction, accelerating potential, and crossed-beam studies, it should be emphasized that the velocity increase is associated with clusters ranging in size from 20 to 100 molecules. Thus, the designation of the pressure at which the velocity increases as the "onset of condensation" (Refs. 2, 6, and 8) may not be strictly correct.

3.3 CLUSTER INTENSITY MEASUREMENTS

Many measurements of the monomer, dimer, trimer, and tetramer intensity in the free-jet expansion of various gases have beem made with quadrupole mass spectrometers (Refs. 2, 3, 7, 8, and 18). The purpose of these measurements has been to determine the kinetics of cluster growth and to establish scaling laws for the onset of condensation.

As noted earlier, considerable attention has been paid to increasing the sensitivity of the quadrupole mass spectrometer so that cluster intensity measurements could be obtained at very low source pressures. During the present investigation, it became apparent that the considerable increase achieved in system sensitivity could not be utilized to obtain cluster intensity measurements at low source pressures. It has been found (Fig. 11) that, at low source pressures, the observed
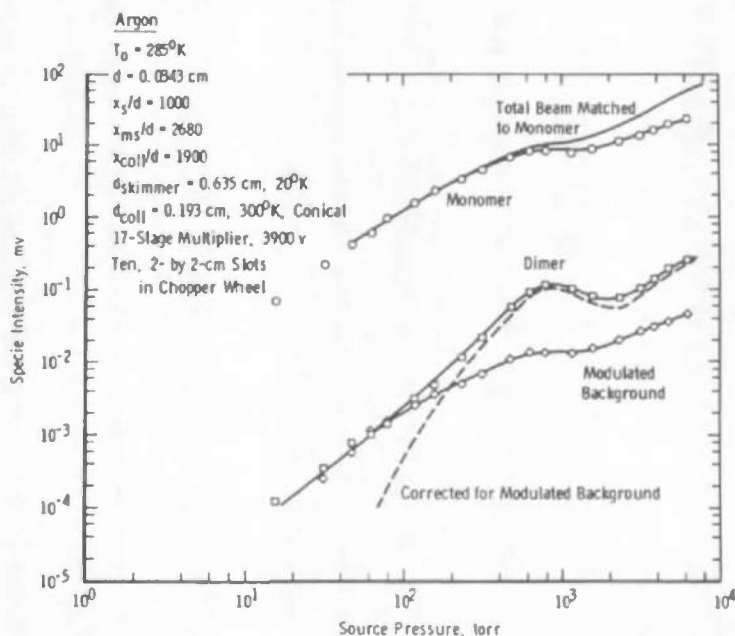

Figure 11. Modulated background signal as a function of source pressure.

modulated beam signal is independent of the mass number to which the mass spectrometer is tuned. The background signal shown in Fig. 11 was obtained by tuning the mass spectrometer to a mass setting not related to argon, its clusters, or doubly ionized particles. It can be seen that, when this signal is subtracted from the dimer signal, the form of the dimer signal at low source pressures is changed significantly. Some limited measurements of cluster intensity have been made utilizing photon counting techniques. (In this mode of operation, the chopper wheel was not used.) It was obvious from these measurements (Fig. 12) that, at low source pressures, the signal was independent of mass setting as was the case for the modulated beam. For the argon and nitrogen data obtained to date, it can be shown that the form of the variation of background signal with source pressure is almost identical to that of the monomer variation with source pressure. This suggests that this background signal is related to the monomer intensity in the bean The fact that it cannot be filtered out in the quadrupole section suggests
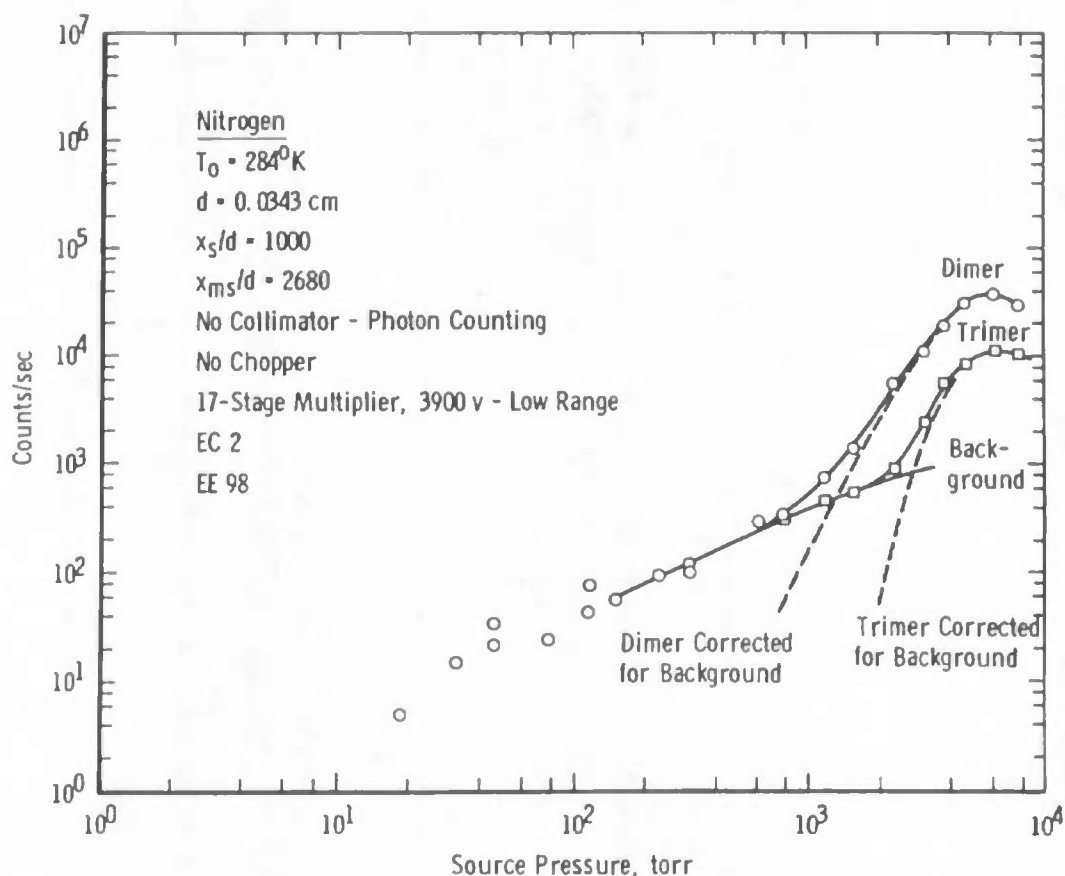

Figure 12. Background signal as a function of source pressure.

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that it is not an ionized particle. There is a strong possibility that this signal results from metastables formed in the ion source, being swept into the quadrupole section by ionized particles. It has been shown (Ref. 10) that metastables are not readily formed in carbon dioxide. Cluster measurements in a carbon dioxide expansion have shown that a background signal of this type does not exist. This observation lends some support to the above suggestion that the background signal is metastable in origin. Fite (Ref. 19) has shown that background signals of the above type can be avoided by offsetting the axis of the multiplier from the axis of the mass filter. In the present investigation, the electron multiplier enclosure was modified such that the axis of the multiplier could be mounted normal to the axis of the mass filter. Unfortunately, within the time scale of the present investigation, it was not possible to resolve successfully the developmental problems resulting from this modification.

There have been a number of modifications to the VKF Aerodynamic Molecular Beam Chamber since the first measurements of this type were made at AEDC-VKF (Refs. 2, 3, and 20). However, the ionizer, mass filter, electron multiplier configuration has remained unchanged throughout all of these other changes. Specie intensity measurements (Fig. 13) obtained in these earlier studies (Refs. 2 and 20) indicate the presence
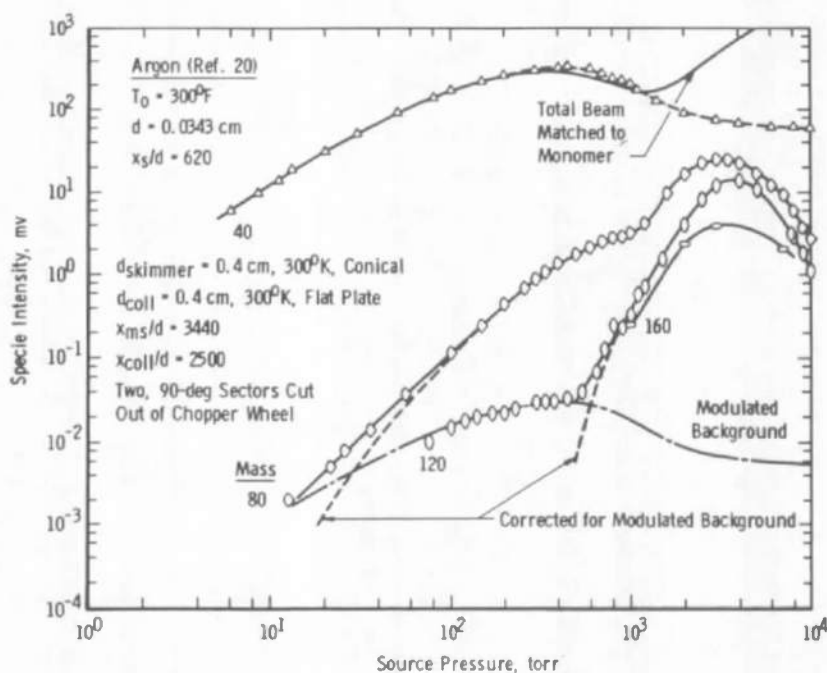

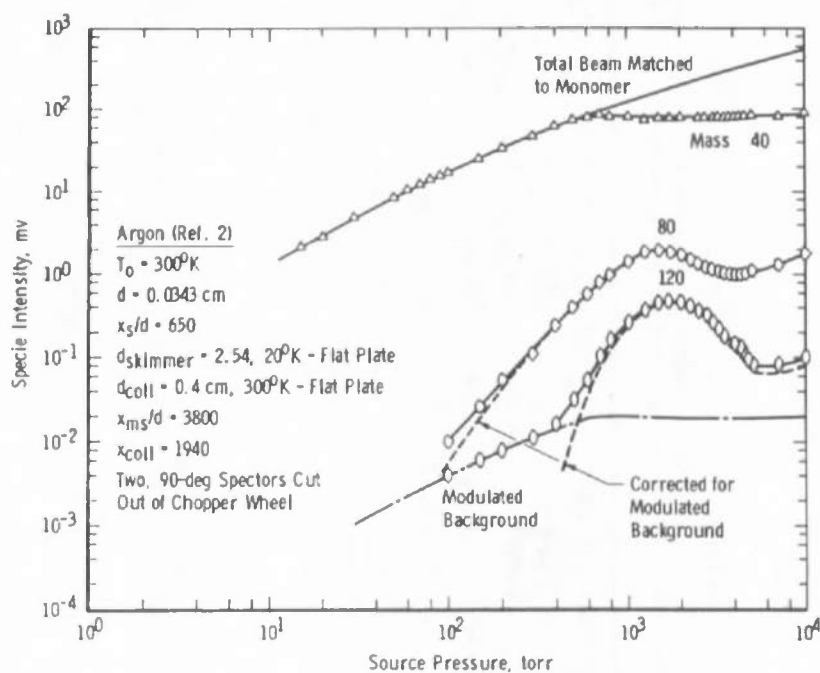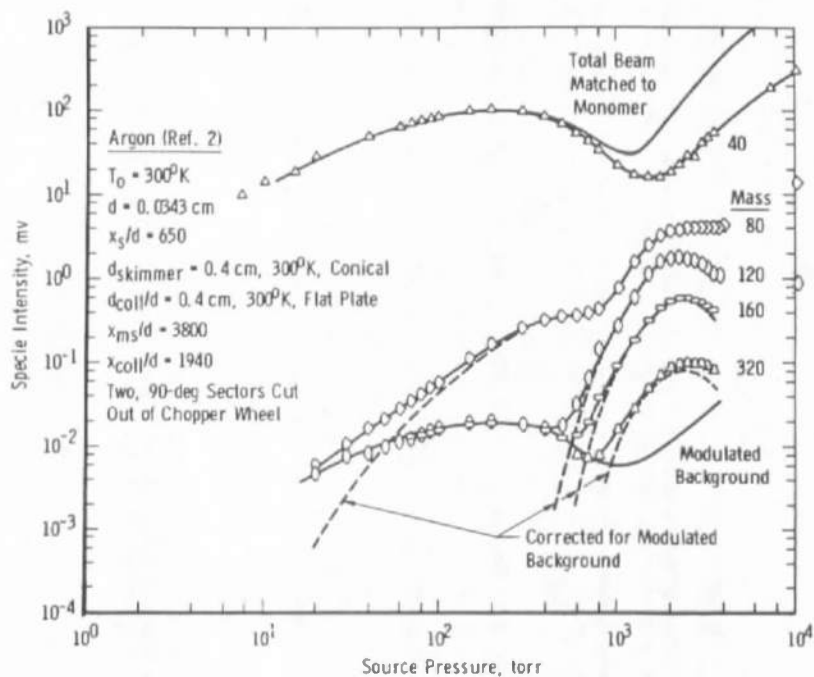Figure 13. Cluster intensity as a function of source pressure.

Figure 13. Concluded.

of a modulated background signal. Unfortunately, the significance of this background signal was not recognized at the time, and the later measurements (Ref. 3), which were aimed primarily at defining the pressure at which the dimer signal peaked, were not affected by this modulated background signal.

Ruby (Ref. 2) observed that cluster intensity measurements in a molecular beam were dominated by skimmer interaction effects. The magnitude of this interaction is illustrated by a comparison of these measurements in Fig. 14. Also shown in Fig. 14 are the dimer and trimer values multiplied by the ratio of the monomer signal obtained with the 20°K skimmer to that obtained with the 300°K skimmer. For pressures less than 700 torr, these scaled values are in good agreement with the 20°K skimmer values. This indicates that, in this pressure regime, the skimmer attenuates beam intensity without significantly affecting the composition of the beam. For pressures greater than 700 torr, the difference between the scaled 300°K skimmer data and the 20°K skimmer data cannot be explained in terms of scattering from the skimmer surface.
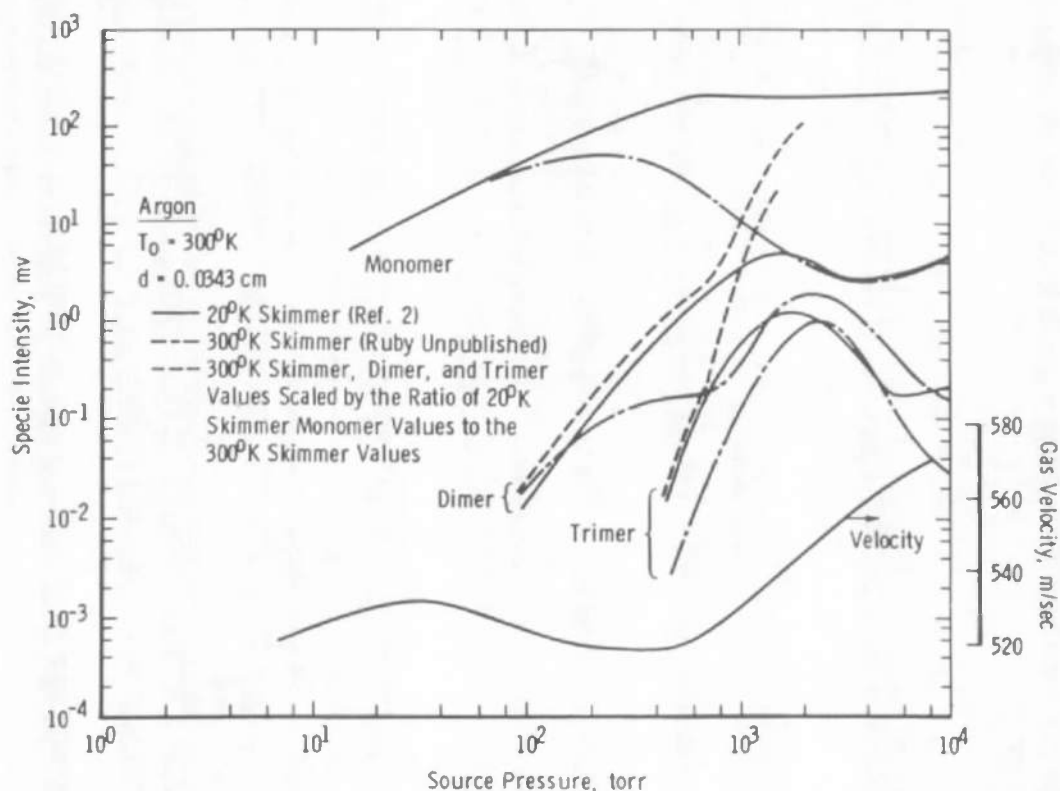
Figure 14. Effect of Skimmer temperature on monomer dimer, and trimer intensity.

It is of interest to note that, at a source pressure of 700 torr, the monomer velocity has started to increase, and as has been mentioned earlier, this increase may be associated with clusters consisting of 20 to 100 molecules. When a beam containing clusters of this size is crossed with an electron beam (i.e., in the ionizer region of a mass spectrometer), the degree of fragmentation will be related to the energy of the electrons.

The effect of electron energy on the dimer intensity observed in a carbon dioxide expansion is shown in Fig. 15. It can be seen that, for

Carbon Dioxide
$T_0 = 217^0K$
$d = 0.0147$ cm
$x_s/d = 1730$
$d_{skimmer} = 1.27$ cm
$d_{coll} = 0.4$ cm

Monomer

Source Pressure at which Velocity Increases from Ref. 6

Electron Energy, v
88

48-v Signal Matched to 88-v Signal
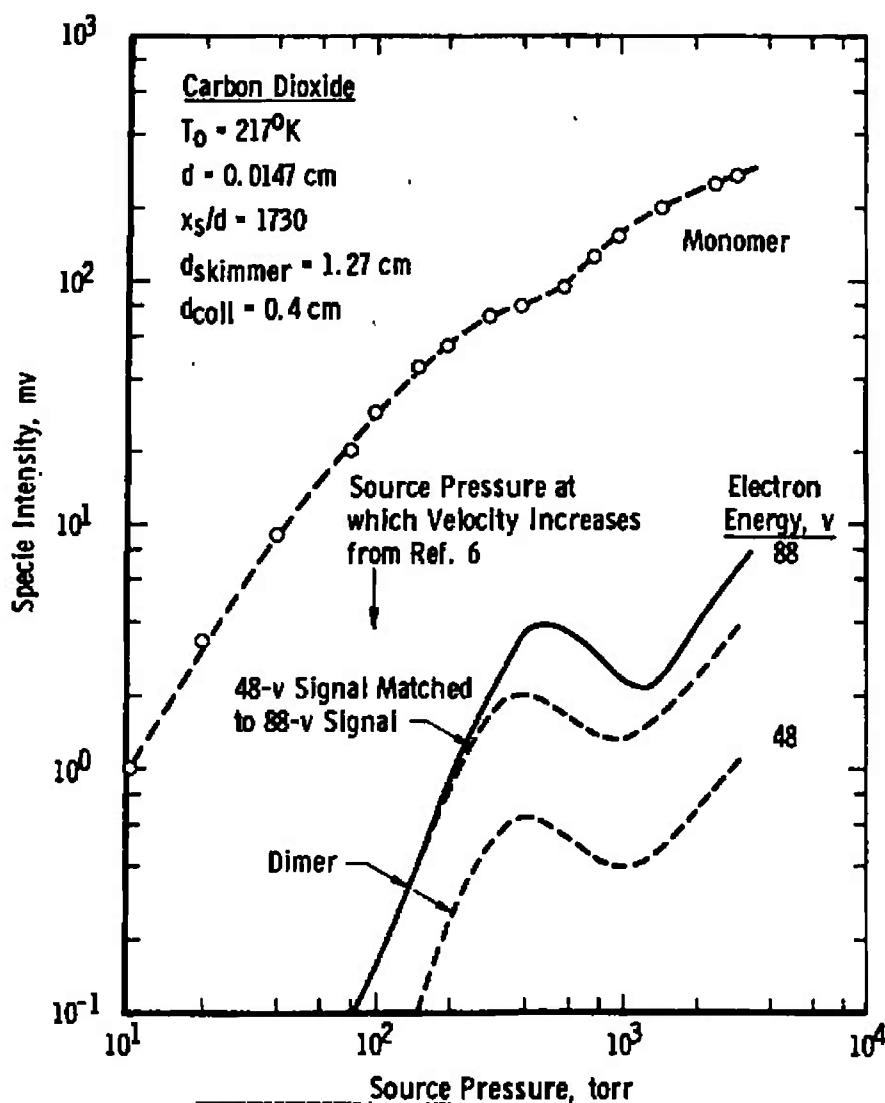
48

Dimer

Source Pressure, torr

Figure 15. Dimer intensity as a function of source pressure and electron energy.

source pressures greater than 200 torr, the increase in dimer intensity with increasing electron energy is greater than for source pressures less than 200 torr. For pressures greater than 200 torr, it is reasonable to assume, on the basis of the above mentioned velocity criterion, that there are large clusters in the beam. Thus, the increment in dimer intensity, illustrated by matching the two dimer signals (Fig. 15), results from fragmentation of larger clusters. Hagena (Ref. 18) has observed this same characteristic in the expansion of room temperature carbon dioxide.

On the basis of these measurements it can be concluded that the observed dimer signal consists of two components, one derived from the dimers in the molecular beam and the other formed by fragmentation of larger clusters in the mass spectrometer. Also, for some warm skimmer configurations (Fig. 14), it has been shown that, for source pressures greater than that at which the velocity increases, the dimer signal is predominantly derived from fragmentation in the mass spectrometer. Some monomer and dimer velocity measurements for a carbon dioxide expansion (Fig. 9) have shown that (1) with a 20°K skimmer the dimer velocity is less than the corresponding monomer velocity, and (2) the monomer and dimer velocities for the 300°K skimmer are less than the corresponding velocities obtained with the 20°K skimmer. These differences are suggestive of differences in velocity of the dimers in the beam and dimers formed from fragmentation of clusters in the mass spectrometer. Some monomer velocity measurements in the free-jet expansion of a low temperature, 85°K, nitrogen beam (Ref. 6) have indicated the presence of fast and slow groups of monomers. It has been postulated that the slow monomers result from fragmentation of large clusters in the ionization region of the mass spectrometer. These measurements indicate that large clusters (on the order of 10^4 molecules) are not accelerated to the speed attained by the noncondensed monomers.

Some velocity measurements obtained by Ruby (Ref. 2) for 20°K and 300°K skimmer are shown in Fig. 16. From an earlier consideration of the specie intensity measurements (Fig. 14), it has been concluded that for the 300°K skimmer the dimer signal results primarily from the fragmentation of large clusters in the ionization section when the source stagnation pressure (p_0) is greater than 700 torr. For $p_0 >$ 1000 torr, the dimer velocity is essentially constant and can be taken to be representative of the velocity at which the parent cluster was formed. If it is assumed that the parent velocity characteristics of a condensation-free argon expansion are known, it can be shown that these clusters are
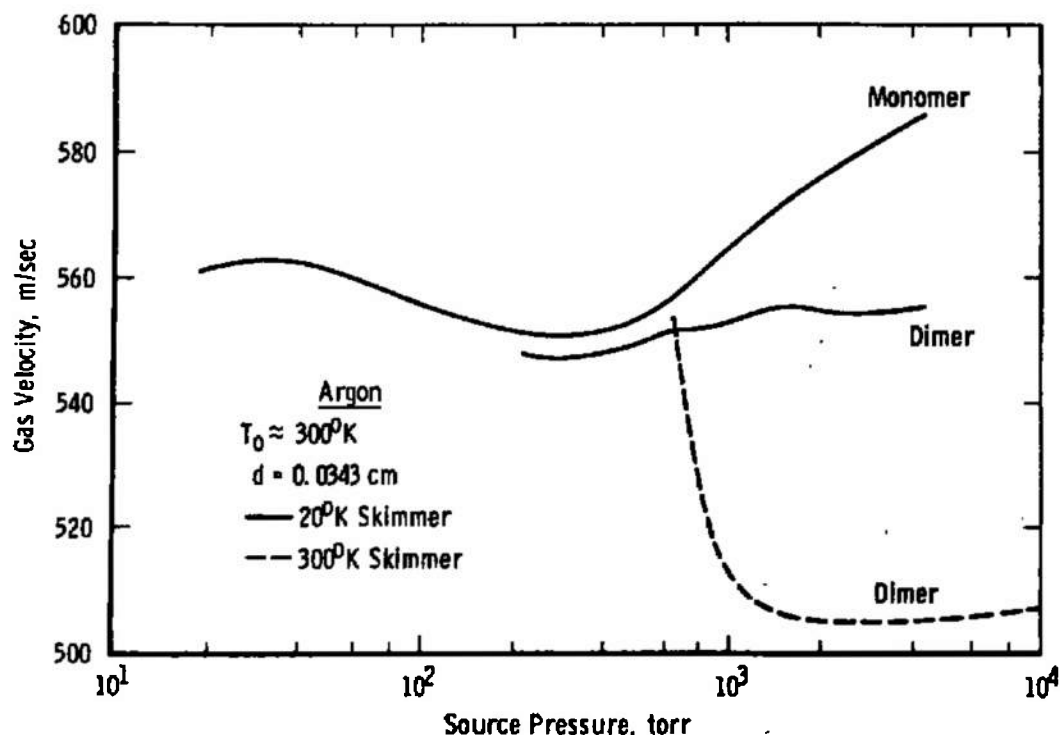
Figure 16. Effect of skimmer temperature on specie velocity.

formed at $M_\infty \approx 3.75$ which occurs at a distance to radius ratio of approximately 1.55. From these dimer velocity measurements, it seems reasonable to conclude that massive condensation occurs for $p_0 > 700$ torr. This is further supported by the dimer velocity measurements made with the 20°K skimmer (Fig. 16). For $p_0 > 600$, the dimer velocity is less than the monomer velocity, indicating an increasing contribution from the fragmentation of large clusters. It can be concluded that the pressure at which the velocity starts to increase is indicative of the occurrence of massive condensation.

One of the criterion suggested in Refs. 7 and 8 as being indicative of condensation is the peak that occurs in the dimer intensity variation with source pressure. It has been shown (Ref. 8) that the pressure at which the dimer signal peaks is determined to some extent by the type of skimmer used to form the molecular beam, i.e., pumping or non-pumping. Golomb, et al (Ref. 8), have shown that the pressure at which the dimer signal peaks for a particular gas is related to the source diameter and temperature. It was recognized in Ref. 8 that part of the mass-ion signals were due to dissociative ionization of large clusters

on electron impact. Dissociative ionization was felt to be particularly important at high source pressures where very large clusters (i.e., greater than 100 molecules) exist. In fact, the secondary rise in the dimer signal has been assumed (Ref. 8) to result from dissociative ionization of the large clusters.

The degree of dissociative ionization, as has been shown earlier (Fig. 15), is related to the energy of the ionizing electrons. For the cluster intensity measurements reported in Refs. 2, 3, 7, 8, and 20, this energy was kept constant at 90 ev.

During the present study, a limited evaluation of the effect of electron energy on cluster signal was made. Measurements of the dimer signal at four discrete electron energies are shown in Fig. 17. As far as possible, all other operating conditions of the mass spectrometer were held constant. A consideration of these measurements indicates that (1) for $p_0 < 500$ torr, the increase of dimer signal with increasing electron energy is independent of source pressure; (2) for $500 < p_0 < 4000$ torr, the increase of dimer signal with increasing electron energy is a function of source pressure; and (3) for $p_0 > 4000$ torr, the dimer signal appears to vary in a similar manner to that observed for $p_0 < 500$ torr.

The form of the dimer signal for $p_0 < 500$ torr and varying electron energy is such that it is reasonable to assume that there is a minimal contribution to the total signal from dissociative ionization. Or, in other words, the measured dimer intensity relates directly to the dimer concentration in the molecular beam sample. This is confirmed by the comparison of the warm and cold skimmer measurements of dimer intensity shown in Fig. 14. For $p_0 < 700$ torr, the monomer, dimer, and trimer measurements are reduced in a similar manner by the presence of the warm skimmer.

For $500 < p_0 < 4000$ torr, the observed dimer intensity contains a significant contribution due to dissociative ionization depending on the electron energy level (Fig. 17). The pressure at which the peak occurs in the dimer signal is a function of the electron energy level (see insert in Fig. 17). With decreasing electron energy, the peak in the dimer signal becomes less and less pronounced, and the pressure at which it occurs approaches the pressure at which the increase in velocity has been observed. Unfortunately, in the present investigation dimer intensity measurements were not made for electron energy levels less than 73 v at this source temperature and diameter. However, some
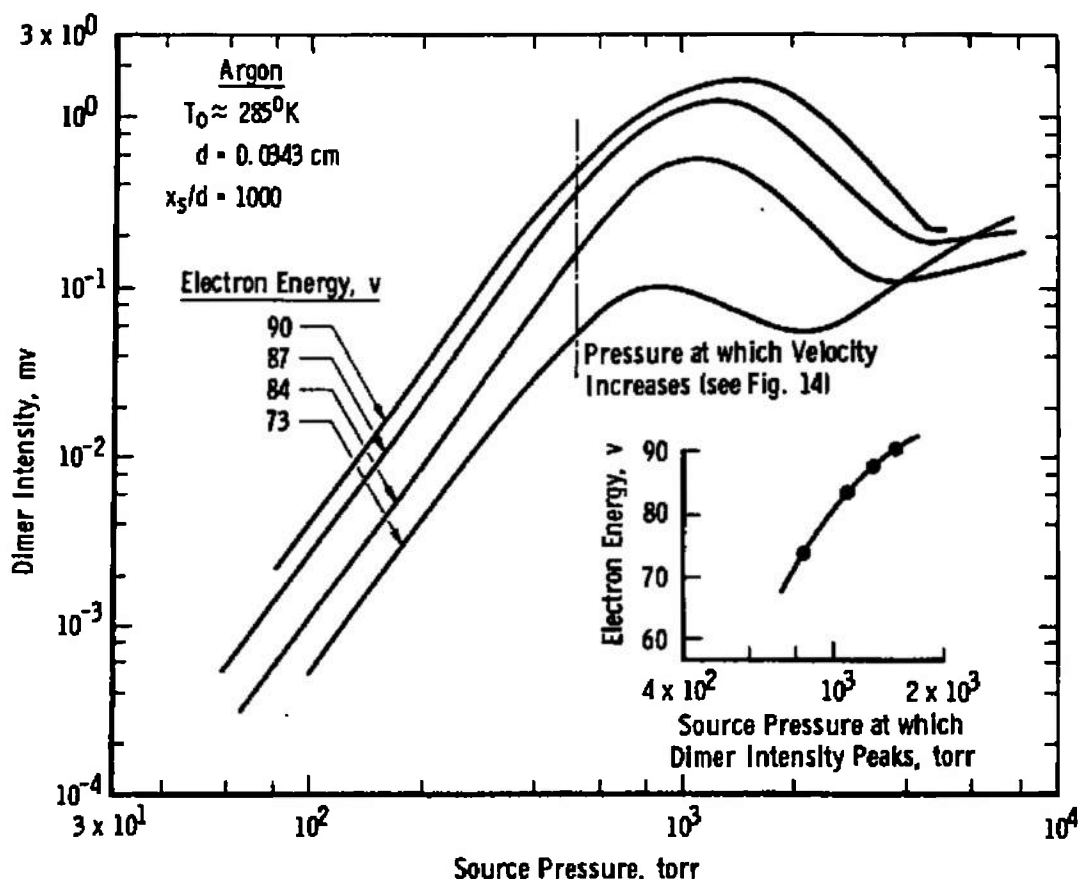
Figure 17. Effect of electron energy on pressure at which dimer signals peaks.

measurements of monomer and dimer intensity for a wider range of electron energy values have been made at different source conditions. The monomer and cluster intensity and velocity variations with source pressure for an electron energy of 90 v are shown in Fig. 18. The source pressures at which the electron energy has been varied, 230 and 1500 torr (Fig. 18), correspond to flow conditions where (1) massive condensation has just occurred and (2) condensation is well developed. At both source pressures, the variation of the monomer and dimer signals with electron energy is similar (Fig. 19). Since large clusters are present in the flow at both source pressures it would seem reasonable to suggest that the increase in signal for electron energies greater than 60 v result from fragmentation of these clusters. However, caution should be exercised in interpretations of this type since Leckenby, et al.(Ref. 21), have observed similar variations at source conditions where there were no large clusters in the flow.
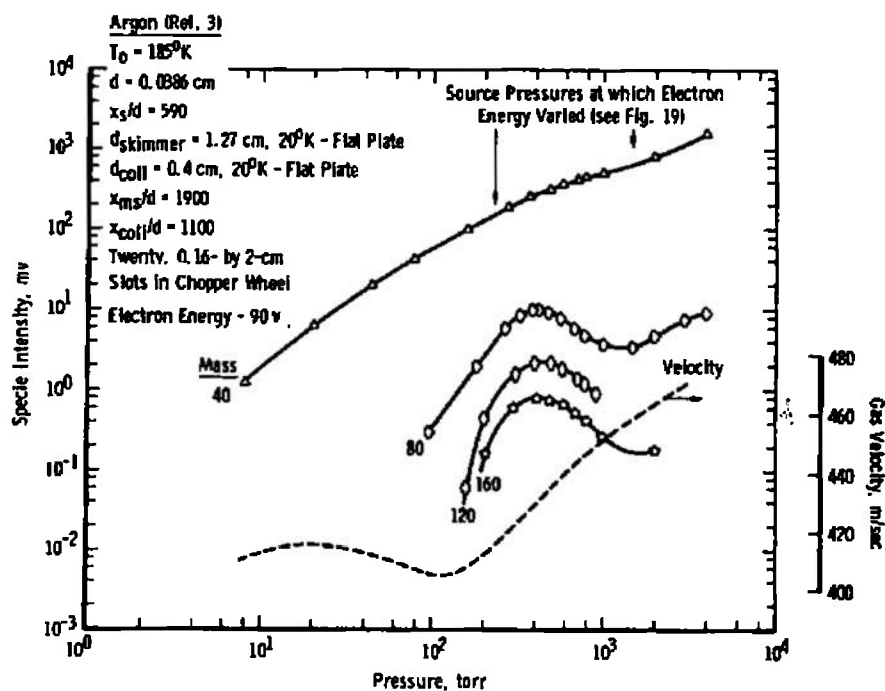
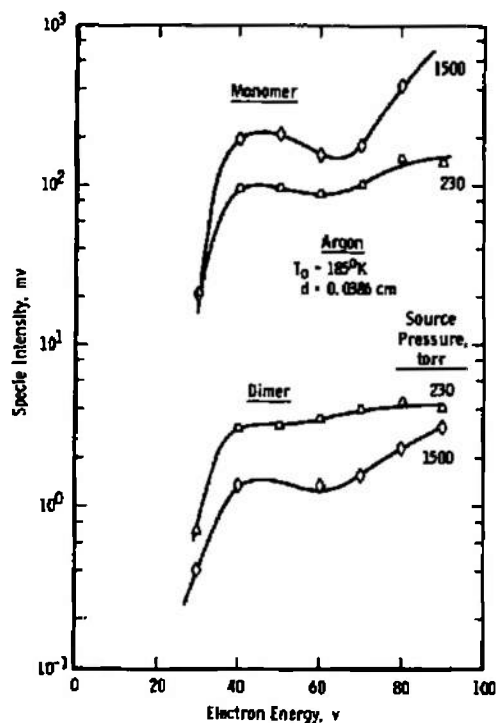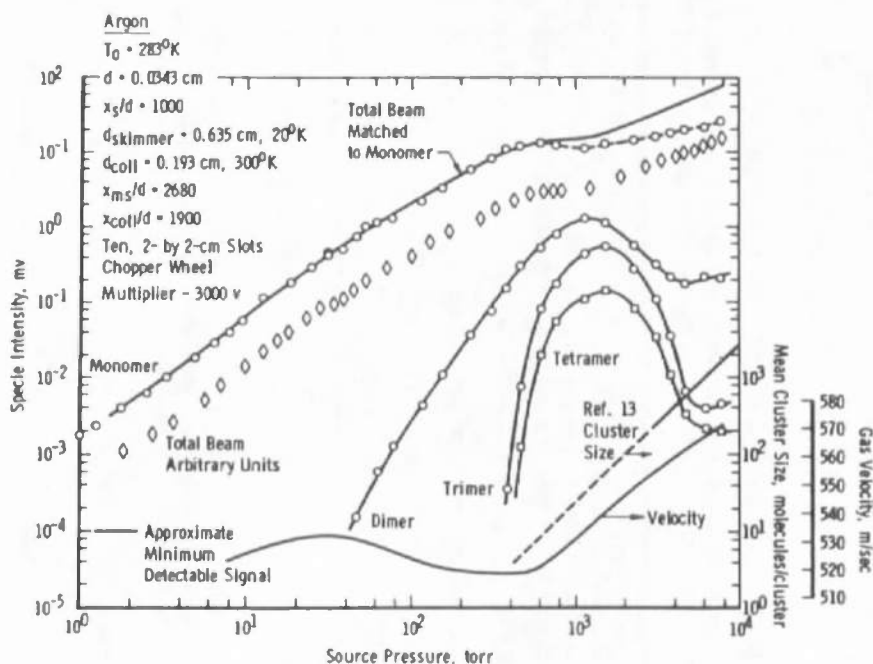**Figure 18. Argon cluster intensity as a function of source pressure.**

Figure 19. Monomer and dimer intensity as a function of electron energy.

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One of the objectives of the present investigation was to obtain measurements of monomer and cluster intensity from which the kinetics of cluster formation may be deduced. Monomer, cluster intensity, and velocity measurements for argon, nitrogen, carbon dioxide, nitric oxide, Krypton, and a 10-percent Krypton/argon mixture are presented in Fig. 20. Where possible, these measurements have been corrected for the mass spectrometer background signal. It is apparent from a consideration of these measurements that there is a significant difference in the form of the dimer and higher mass cluster variation with source pressure. The trimer and tetramer intensity variation with source pressure is such that their appearance in the expansion process appears to be related to the observed increase in gas velocity (Figs. 20a, b, and c) which in turn suggests that their onset is related to the onset of massive condensation in the flow.
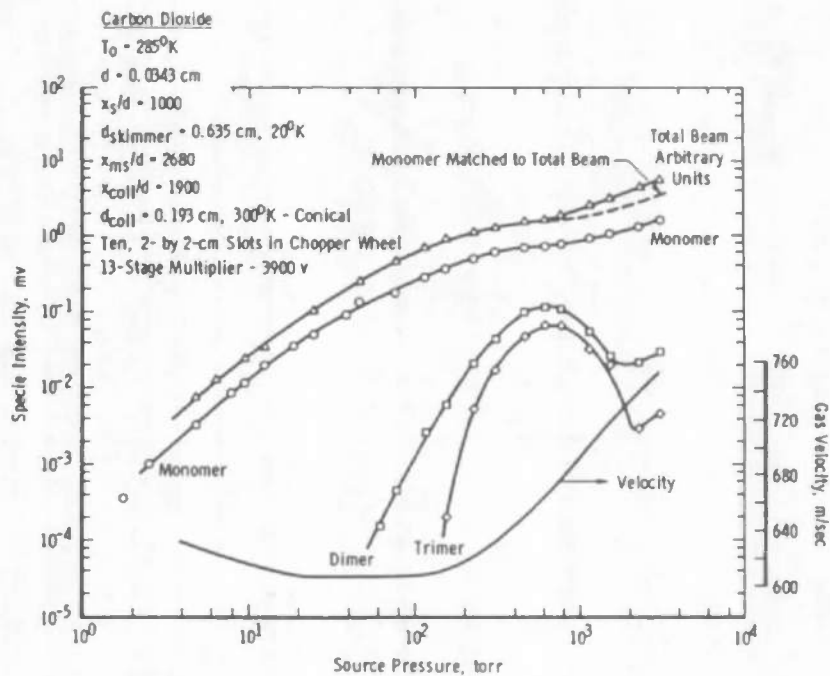

a. Argon

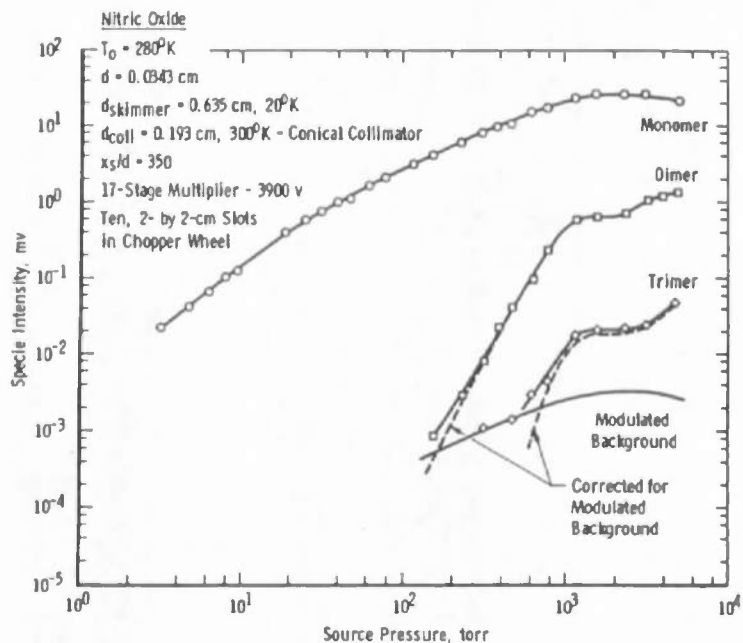Figure 20. Cluster intensity as a function of source pressure for various gases.
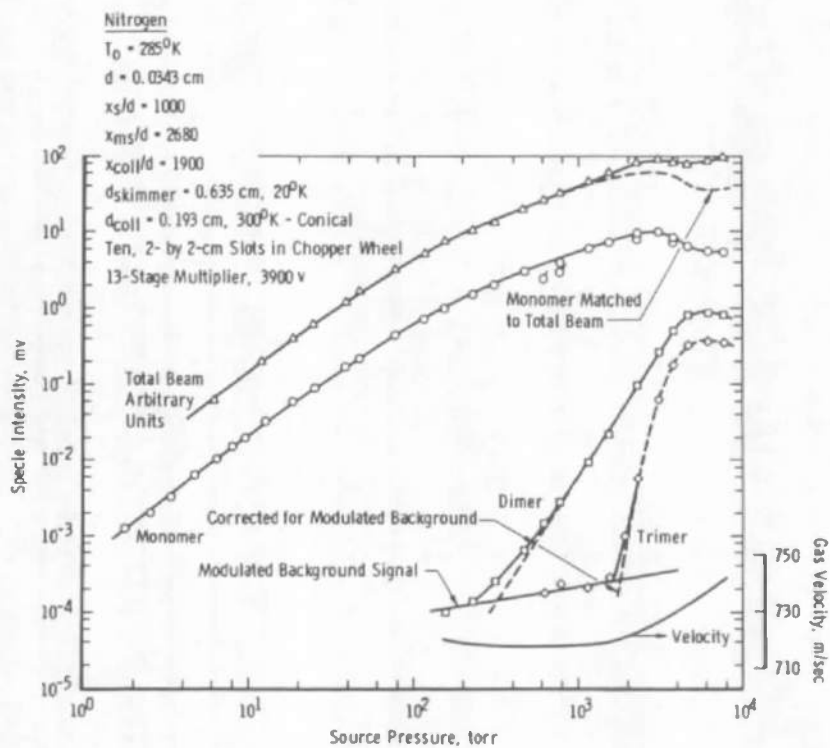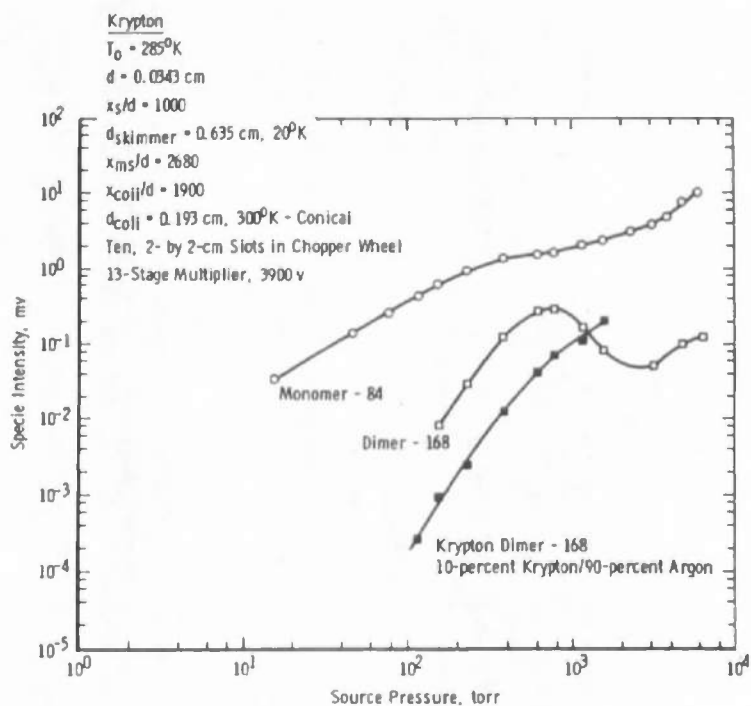
b. Nitrogen

c. Carbon dioxide

Figure 20. Continued.

d. Nitric oxide

e. Krypton

Figure 20. Concluded.